

# Luminescence properties of samarium-doped SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> composite

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## Abstract

The comprehensive structural and luminescence study of Sm-doped SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> composite materials are reported. The samples were synthesized by melt-mixing mixture of Na<sub>2</sub>SO<sub>4</sub> and SmF<sub>3</sub> into the SiO<sub>2</sub> matrix at 1050°C for 30 min. X-ray diffraction (XRD) pattern shows the characteristic structure of the SiO<sub>2</sub> and addition of 20% Na<sub>2</sub>SO<sub>4</sub>:Sm has no effect on the basic crystal structure of the SiO<sub>2</sub>. Scanning electron microscopy (SEM) shows the clear difference in morphological structure between the composite and host SiO<sub>2</sub>. From photoexcitation (PE) spectra of the as-synthesized composite, the highest excitation efficiency was observed at 402 nm. The photoluminescence (PL) spectra of as-synthesized composite phosphors obtained under 402 nm excitation consist of five narrow emission bands with peaks at 563, 598, 644, 704 and 784 nm. These are assigned to the <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>J</sub> (J=5/2, 7/2, 9/2, 11/2 and 13/2, respectively) transitions within 4f<sup>5</sup> electronic configuration of Sm<sup>3+</sup>. Highest luminescence intensity was observed with SiO<sub>2</sub>-10%Na<sub>2</sub>SO<sub>4</sub>:Sm.

**Keywords:** SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>, Luminescence, Sm

## 1. Introduction

The luminescence properties of the lanthanide ion-doped materials have been hot research topic for decades. An attractive feature of luminescent rare earth ions is their line-like emission and this emission is largely independent of the host environment[1]. This characteristic of lanthanide ions make it very attractive for synthesizing various kinds of functional materials for application. Recently, there has been a strong interest in synthesis of lanthanide based organic-inorganic hybrid materials [2, 3], glass-ceramic phosphor[4, 5, 6] and composite materials[7, 8] for a wide variety of application in outdoor devices, fabrication of light emitting diodes, scintillators, and optical devices. SiO<sub>2</sub> is known for its hardness and used primarily for production of various kinds of glass materials. This is also very suitable host for synthesizing composite materials. Luminescence properties of lanthanide ions doped Na<sub>2</sub>SO<sub>4</sub> were reported elsewhere[9, 10, 11]. Embedding rare earth doped-Na<sub>2</sub>SO<sub>4</sub> phosphor in ceramic materials such as SiO<sub>2</sub> may increase the strength of the phosphor, especially when designed for outdoor application. A composite of SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> can be useful for high-temperature thermal storage. Thermophysical properties of this composite are investigated[12]. S. M. Bobade et. al. reported on the electrical properties of the Na<sub>2</sub>SO<sub>4</sub>-based composite system[13]. However, very few works were done on the rare earth doped SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> phosphor[14]. There was no

work reported on luminescence properties of Sm-doped SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> system to the best of our knowledge. In the present study, we synthesized Sm-doped SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> composite material and obtained the PL and PE spectra of the Sm<sup>3+</sup> ions.

## 2. Experimental

High purity SiO<sub>2</sub> (99%), Na<sub>2</sub>SO<sub>4</sub> (99.99%) and SmF<sub>3</sub>(99.99%) were used to synthesize samples. A mixture of Na<sub>2</sub>SO<sub>4</sub> and small amount of SmF<sub>3</sub> (0.14 mol%) was ground using an agate mortar. This mixture in appropriate amount (5, 10 and 20 percent mass of the host SiO<sub>2</sub>) was again thoroughly mixed with SiO<sub>2</sub> and ground by agate mortar. The mixtures were then heated in pure alumina crucibles at 1050°C for 30 min in air by using an electric furnace. Samples were quenched to room temperature (RT) by placing on a lead brick after heating. Synthesized samples were powdered again for performing measurements. Crystal structures of the samples were examined using XRD system ( 12kW Rigaku D-Max-rA X-ray diffractometers) at RT with CuK $\alpha$ <sub>1</sub> radiation operating at 40 kV and 100 mA. A SEM measurement was performed using a Hitachi model S-4800 field emission scanning electron microscope. A small amount of powder samples were sprinkled lightly with a spatula on carbon tape and pressed lightly for mounting.

Measurement of PL and PE spectra were performed at RT by using a totally computer-controlled compact system (Horiba Fluorolog spectrofluorometer). PL intensity measurements were done strictly maintaining the same conditions for each sample. All the intensity measurements were repeated 10 times and an average was taken to reduce error.

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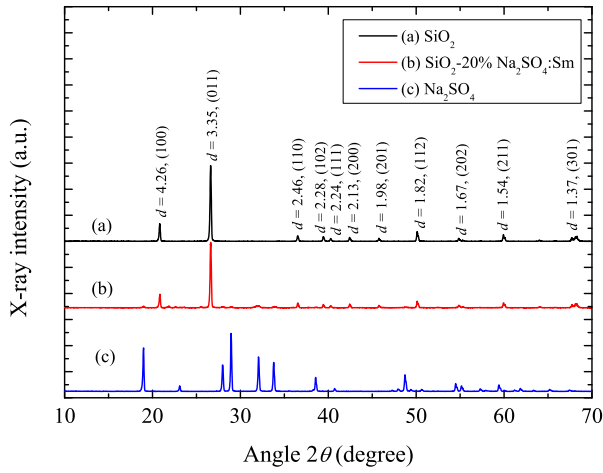


Figure 1: (Color online) XRD spectra of (a) SiO<sub>2</sub> (b) SiO<sub>2</sub>-20%Na<sub>2</sub>SO<sub>4</sub>:Sm and (c) Na<sub>2</sub>SO<sub>4</sub>.

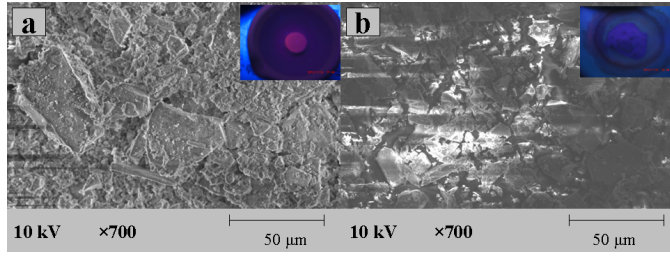


Figure 2: (Color online) SEM image of (a) SiO<sub>2</sub>-20%Na<sub>2</sub>SO<sub>4</sub>:Sm composite, inset: synthesized composite shows red emission under UV light (b) SiO<sub>2</sub>, inset: no emission from host under UV light.

### 3. Results and discussion

Figure 1 shows the XRD patterns for SiO<sub>2</sub>, SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>:Sm, Na<sub>2</sub>SO<sub>4</sub>:Sm and Na<sub>2</sub>SO<sub>4</sub>. The main diffraction peaks were in good agreement with the data of ICDD card 37-1465 and JCPDS standard pattern number 46-1045 for Na<sub>2</sub>SO<sub>4</sub> and SiO<sub>2</sub>, respectively. SiO<sub>2</sub> has hexagonal crystal structure with  $P3_221$  space group. The  $(h\ k\ l)$  values and  $d$ -values were shown in XRD spectra. The values were calculated by using PowderX software[15]. The lattice parameters of the unit cell of SiO<sub>2</sub> were  $a = b = 4.9137\text{ \AA}$  and  $c = 5.4047\text{ \AA}$  with  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$ . From Fig. 1, it is clear that the phosphor particles were well incorporated between the SiO<sub>2</sub> particles.

The particle size  $d$  can be estimated from the Scherrer equation as follows:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where  $\lambda$  is the wavelength of the CuK $_{\alpha 1}$  radiation,  $\beta$  is the full-width at half-maximum (FWHM) at radian and  $\theta$  is the diffraction angle. Most prominent diffraction peaks at 20.82, 26.62 and 50.12 were taken to measure the particle size. Average particle size of the SiO<sub>2</sub> powder and SiO<sub>2</sub>-20%Na<sub>2</sub>SO<sub>4</sub>:Sm composite powder was estimated to be 56 nm.

Fig. 2 shows the SEM image of the (a) SiO<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>:Sm composite and (b) SiO<sub>2</sub>. Inset shows the red emission under UV

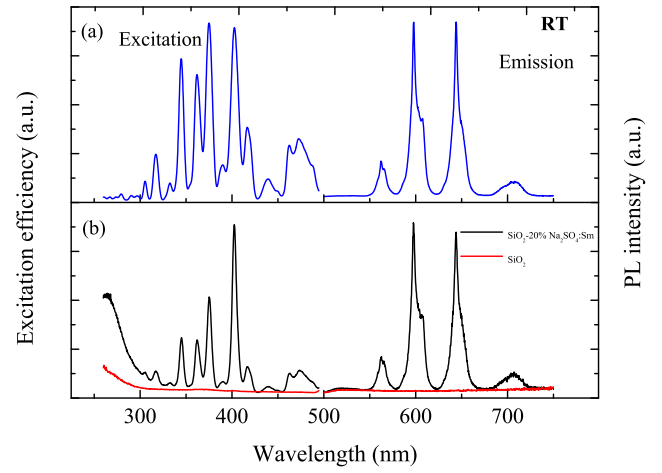


Figure 3: (Color online) (a) PE (left) and PL spectra (right) of Na<sub>2</sub>SO<sub>4</sub>:Sm. (b) PE (left) and PL (right) spectra of SiO<sub>2</sub>-20%Na<sub>2</sub>SO<sub>4</sub>:Sm. Excitation and emission spectra (red line) for SiO<sub>2</sub> was given for comparison. Observation wavelength: 644 nm. Excitation wavelength: 375 nm.

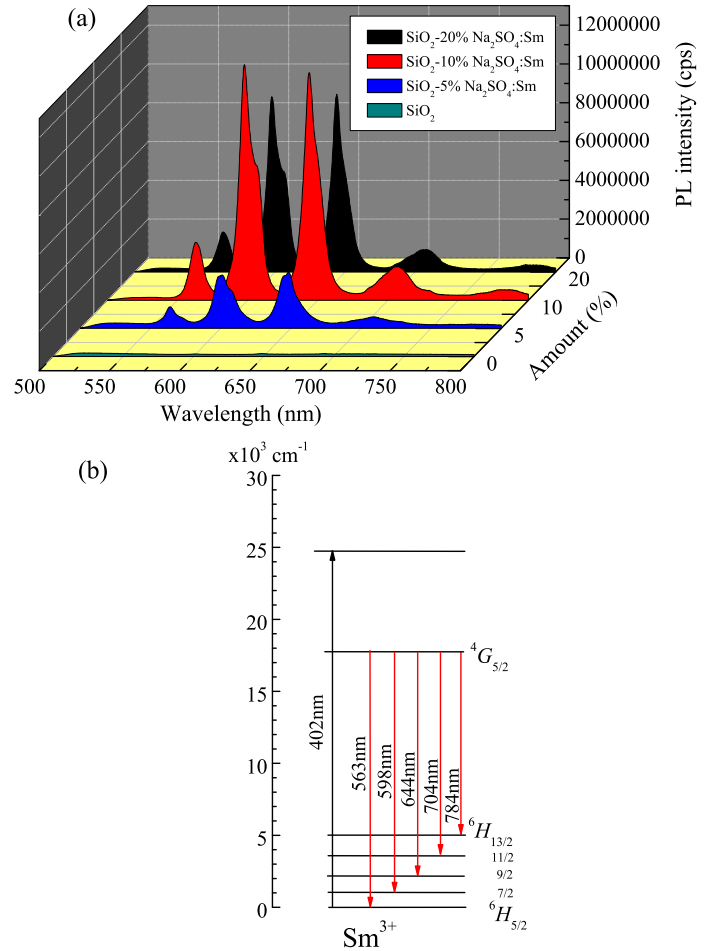


Figure 4: (Color online) (a) PL spectra of SiO<sub>2</sub>- $x$ %Na<sub>2</sub>SO<sub>4</sub>:Sm ( $x=0,5,10,20$ ) under excitation at 402 nm. (b) Schematic energy levels of Sm<sup>3+</sup> ( $4f^5$ ) in composite materials. Arrows show the excitation and emission transitions.

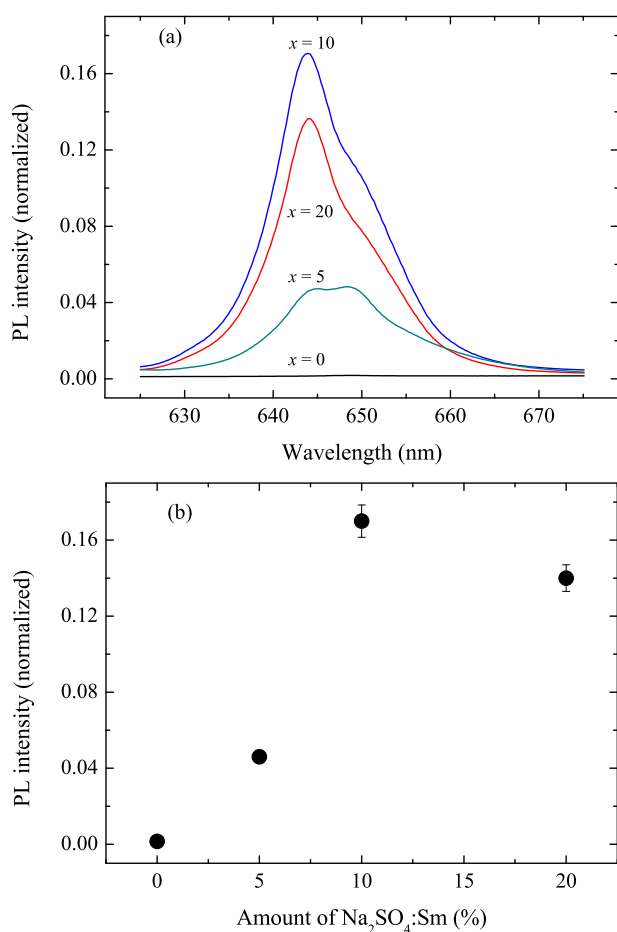


Figure 5: (Color online) (a) PL spectra of 644 nm band under 402 nm excitation for  $\text{SiO}_2$  and  $\text{SiO}_2$ - $x\%\text{Na}_2\text{SO}_4:\text{Sm}$  ( $x=5,10,20$ ). (b) Relative PL intensities of the 644 nm band.

light in Sm doped  $\text{SiO}_2$ - $\text{Na}_2\text{SO}_4$  composite material whereas no emission under UV light in host  $\text{SiO}_2$ . SEM images were magnified 700 times for both samples. It is clearly seen that morphological structures are different in Sm-doped  $\text{SiO}_2$ - $\text{Na}_2\text{SO}_4$  and  $\text{SiO}_2$ . Particle size was measured to be 50 nm for both  $\text{SiO}_2$  and  $\text{SiO}_2$ -20% $\text{Na}_2\text{SO}_4:\text{Sm}$ , which is in good agreement with that estimated from diffraction peaks (fig. 2).

Figure 3(a) shows the PE (left) and PL (right) spectra of  $\text{Na}_2\text{SO}_4:\text{Sm}$  phosphor. The PL spectrum, obtained under 375 nm excitation, consists of four narrow bands at 563, 598, 644 and 704 nm. The excitation spectrum was obtained by monitoring the red luminescence at 644 nm. Figure 3(b) shows the PE (left) and PL (right) spectra of the  $\text{SiO}_2$ -20% $\text{Na}_2\text{SO}_4:\text{Sm}$  composite and  $\text{SiO}_2$  (red line). Measurement condition was same as that of  $\text{Na}_2\text{SO}_4:\text{Sm}$  phosphor. No disturbance due to host was observed in the PL spectra, as  $\text{SiO}_2$  has no obvious emission at the range 500-750 nm, where main  $\text{Sm}^{3+}$  emission peaks appear. From PE spectra the highest excitation efficiency was observed at 375 nm for  $\text{Na}_2\text{SO}_4:\text{Sm}$  whereas 402 nm for  $\text{SiO}_2$ -20% $\text{Na}_2\text{SO}_4:\text{Sm}$ .

Figure 4(a) shows the PL spectra of the  $\text{SiO}_2$ - $x\%\text{Na}_2\text{SO}_4:\text{Sm}$

( $x = 5, 10, 20$ ) under 402 nm excitation which consist of five narrow bands at 563, 598, 644, 704 and 784 nm. These five bands can be identified with the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$  ( $J=5/2, 7/2, 9/2, 11/2$  and  $13/2$ , respectively) transitions within  $4f^5$  electronic configuration of  $\text{Sm}^{3+}$  (Fig. 4(b)). Trivalent samarium ions with  $4f^5$  are generally insensitive to the surrounding environment in the crystal, due to outer shell shielding. Nevertheless, emission spectra are still influenced by the Stark effect caused by the crystal field and asymmetry around the  $\text{Sm}^{3+}$ . Emission bands observed in Sm-doped  $\text{SiO}_2$ - $\text{Na}_2\text{SO}_4$  composite are almost same as that of  $\text{Na}_2\text{SO}_4:\text{Sm}$ . So it is reasonable to assume that  $\text{Sm}^{3+}$  ions take the position in the composite by replacing  $\text{Na}^+$  ions in  $\text{Na}_2\text{SO}_4$ .

PL spectra of the prominent 644 nm band was measured 10 times for each sample to measure relative intensities (Fig. 5(b)). Average intensity was taken to minimize the intensity error. From the Fig. 5(b) it is shown that with increase in the phosphor amount, the PL intensity of 644 nm band was also increased. When 20% phosphor was used, the PL intensity decreased a little. So the highest PL intensity was obtained from  $\text{SiO}_2$ -10% $\text{Na}_2\text{SO}_4:\text{Sm}$ . PL intensity of this sample was found to be approximately 17% comparing to that of  $\text{Na}_2\text{SO}_4:\text{Sm}$ . This is reasonable and better PL efficiency because the amount of  $\text{SmF}_3$  in  $\text{SiO}_2$ -10% $\text{Na}_2\text{SO}_4:\text{Sm}$  is only 0.014 mol% whereas 0.14 mol% (10 times amount compare to that of  $\text{SiO}_2$ -10% $\text{Na}_2\text{SO}_4:\text{Sm}$ ) in  $\text{Na}_2\text{SO}_4:\text{Sm}$  phosphor.

#### 4. Conclusion

We have successfully synthesized samarium doped  $\text{SiO}_2$ - $\text{Na}_2\text{SO}_4$  composite. It may strengthen the  $\text{Na}_2\text{SO}_4:\text{Sm}$  phosphors embedded in  $\text{SiO}_2$  matrix. We believe this composite has good prospect as a phosphor material for variety of application such as light emitting diodes, outdoor application, scintillators.

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#### References

- [1] Koen Binnemans. Chem. Rev. 2009; 109: 4283-4374.
- [2] S. B. Mishra, A. K. Mishra, N. Revaprasadu, K. T. Hillie, W. J. vdM. Steyn, E. Coetsee, H. C. Swart. J. Appl. Polym. Sci. 2009; 112: 3347-54.
- [3] Purificacion Escribano, Beatriz Julian-Lopez, Jose Planelles-Arago, Eloisa Cordoncillo, Bruno Viana, Clement Sanchez. J. Mater. Chem. 2008; 18: 23-40.
- [4] Shunsuke Fujita, Akihiko Sakamoto, Setsuhisa Tanabe. IEEE Journal of Selected Topics in Quantum Electronics 2008; 14: 1387-91.
- [5] I. Sabikoglu, M. Ayvackl, A. Bergeron, A. Ege, N. Can. J. Lumin. 2012; 132: 1597-1602.
- [6] G. Belev, G. Okada, D. Tonchev, C. Koughia, C. Varoy, A. Edgar, T. Wysokinski, D. Chapman, S. Kasap. Phys. Status Solidi C 2011; 8: 2822-25.
- [7] Yanbin Zhang, Zhenfeng Zhu, Yinpo Qiao. Mater. Lett. 2013; 93: 9-11.
- [8] Steven C. Allen, Andrew J. Steckl. Appl. Phys. Lett. 2008; 92: 143309 (1-3).

- [9] A. Sidike, A.Z.M.S. Rahman, J.-Y. He, K. Atobe, N. Yamashita. *J. Lumin.* 2009; 129: 1271-75.
- [10] A. Sidike, A.Z.M.S. Rahman, J.-Y. He, L.-X. Gong, K. Atobe, N. Yamashita. *J. Lumin.* 2011;131: 1840-47.
- [11] A. Z. M. S. Rahman, X. Cao, L. Wei, B. Wang, R. Yu, Z. Chen, G. An, A. Sidike. *Appl. Phys. A* 2012; DOI 10.1007/s00339-012-7266-y.
- [12] W. Notter, Th. Lechner, U. Grob, E. Hahne. *Thermochimica Acta* 1993; 218: 455-63.
- [13] S. M. Bobade, A. R. Kulkarni, P. Gopalan. *Ionics* 2007; 13: 257-62.
- [14] L. I. Anikina, T. S. Dobrolyubskaya, A. V. Karyakin, Viet Le Binh. *J. Appl. Spectros.* 1969; 10: 353-54.
- [15] C. Dong. *J. Appl. Cryst.* 1999; 32: 838-839.